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**WO 01/73424 A1**

**(54) Title:** **METHOD AND APPARATUS FOR THE DOWN-HOLE CHARACTERIZATION OF FORMATION FLUIDS**

**(57) Abstract:** Disclosed is a formation fluid analysis module which utilizes a down-hole gas and/or liquid chromatography to determine the molecular constituents of formation fluids, as distinguished from drilling contaminants, and to provide information about the physical and chemical properties of the sample.

PATENT SPECIFICATION

TITLE: METHOD AND APPARATUS FOR THE DOWN-HOLE  
5 CHARACTERIZATION OF FORMATION FLUIDS

10

BACKGROUND OF THE INVENTION1. Field of the Invention

The present invention relates to methods and apparatus for analyzing the subterranean. In another aspect, the present invention relates to methods of and apparatus for analyzing formation fluids and gases. In even another aspect, the present invention relates to distinguishing formation fluids and gases from drilling 15 contaminates in methods of and apparatus for analyzing formation fluids and gases. In still another aspect, the present invention relates to utilizing chromatography in methods of and apparatus for analyzing formation fluids and gases. In yet another aspect, the present invention relates to methods and apparatus for analyzing formation 20 fluids and gases, utilizing tags or markers in the well fluid. In still another aspect, the present invention relates to methods and apparatus for analyzing formation fluids and gases, utilizing tags or markers in the well fluid.

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## 2. Description of the Related Art

Hydrocarbon exploration and data gathering of wells can be accomplished by utilizing wireline logs or logging while drilling tools (LWD) to obtain certain physical characteristics of a formation. Wireline logs require an umbilical (e.g. wireline, tool push-in, coiled tubing) from the surface to provide electrical power and are generally utilized after a well is drilled. LWDs are used to provide quantitative analysis of sub-surface formations during the actual drilling operation. LWDs typically include their own power source as the LWD string is an integral part of the bottom hole assembly and it would be impractical to connect an umbilical from the surface to provide electrical power or other requirements of the various LWD tools.

The formation characteristics monitored by wireline logs and LWDs can include formation density, porosity, and water saturation. However, more detailed analysis would aid in characterization of a formation.

The analysis of the physical properties of the formation fluids, for example to determine relative amounts of oil, gas, and water, and the density, viscosity and compressibility of the fluid, is also of importance in determining the physical properties of a particular well.

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However, the means of analysis of such formation fluids must be able to discriminate between the formation fluids and any drilling fluid components mixed with or intermingled with the formation fluids. For example, the 5 hydrocarbon and/or water phases of the sample fluid may be contaminated with hydrocarbon and/or water components from the drilling fluid and/or mud filtrate.

For example, typically, the drilling fluids or muds will be either water or oil based. While oil base fluids are particularly useful in unconsolidated and water-susceptible formations, the hydrocarbons present in the drilling fluid may mask the formation fluids in the drilling mud returns, thus preventing the identification 10 of formation hydrocarbons.

Likewise, even when water based muds are used, diesel or other hydrocarbons may be added to aid in lubricating the drill bit, and likewise cause a similar masking of formation hydrocarbons. Furthermore, the water of the water based mud may mask the formation water 15 phase, and cause a distortion of the formation hydrocarbon/water ratio.

The quantitative analysis of the constituents of the formation fluid distinguished from drilling fluids can be accomplished by obtaining reservoir samples, which are 20 taken to the laboratory and subjected to chromatography, 25

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either gas or liquid, which are a known analytical techniques.

Present methods and apparatus require that a sample be removed from the well and analyzed by chromatography either at the well site or remote to it.

5

In some instances, no steps are taken to maintain the sample at the high pressures of the subterranean form which it was sampled, which may cause a phase change in part or all of the sample, and possibly skewing the results of any analysis. For while the sample may later 10 be "repressurized," there may be hysteresis effects that come into play resulting in different composition results, or some or all of the sample may be "lost" through "venting" bringing it to the surface, and may 15 skew the results.

15

In other instances, while steps are taken to maintain the sample at the high pressures of the subterranean form which it was sampled, at some point (i.e., as a non-limiting example, during transfer from 20 the sample container to an analyzer) the sample pressure may be reduced, which again, may possibly skew the results of any analysis.

20

Furthermore, even with advanced chromatography techniques, it is still sometimes difficult to

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distinguish in the sample, contributions by formation fluids from contributions by drilling fluids.

An extremely large number of patents exist directed to chromatography, see for example, U.S. Patent Nos. 5,856,616, 5,918,273, 5,980,834, 6,004,514, 6,035,697, all herein incorporated by reference.

Portable units for gas chromatography are known. U.S. Patent No. 5,980,832, issued, November 9, 1999 to Andresen , et al. for an ultratrace detector for hand-held gas chromatography, herein incorporated by reference.

See also, U.S. Patent No. 5,980,832, issued November 9, 1999, to Andresen et al., and herein incorporated by refernce, which discloses that a hand-held (portable) gas chromatographic oven and pancake capillary gas chromatographic column has been developed for fast gas chromatographic analysis of industrial gases. While many uses are suggested for this new hand held gas chromatographic detector, such as, for industry, drug detection for DEA, very sensitive flammable gas detector, chemical and biological weapons monitoring, pollution monitoring, nuclear proliferation signatures, in-line monitoring for gas and oil refineries, solvent monitoring in electronic industries, stack emission control and

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monitoring, and even for oil well alarms, use of such an instrument down hole is not disclosed or suggested.

Additionally, miniature chromatography systems are known. See, for example, U.S. Patent No. 6,033,628, issued March 7, 2000, to Kaltenbach, et al., for miniaturized planar columns for use in a liquid phase separation apparatus. Kaltenbach et al. invention relates to miniaturized planar column technology for liquid phase analysis, and more particularly to fabrication of microstructures in novel separation support media using laser ablation techniques. According to Kaltenbach et al, their microstructures find use in any analysis system which may be performed on small and/or macromolecular solutes in the liquid phase and which may employ chromatographic or electrophoretic means of separation. Kaltenbach further notes that several approaches towards miniaturization for liquid phase analysis have developed in the art; the conventional approach using drawn fused-silica capillary, and an evolving approach using silicon micromachining.

Further according to Kaltenbach, in conventional miniaturized technology the instrumentation has not been reduced in size; rather, it is the separation compartment size which has been significantly reduced. Kaltenbach notes as an example, micro-column liquid chromatography

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(.mu.LC) wherein columns with diameters of 100-200 .mu.m are employed as compared to prior column diameters of around 4.6 mm.

Another approach towards miniaturization noted by 5 Kaltenbach et al., has been the use of capillary electrophoresis (CE), which entails a separation technique carried out in capillaries 25-100 .mu.m in diameter. CE has been demonstrated to be useful as a method for the separation of a variety of large and small 10 solutes.

Chromatography systems for analyzing hydrocarbon and especially in-line analysis of hydrocarbons are known. See, for example, U.S. Patent No. 6,000,274, issued December 14, 1999 to Lai et al., discloses a 15 chromatography method and apparatus for automatically detecting total hydrocarbon content and individual volatile organic compound concentrations of waste gas, and notes that various on-line waste-gas-detecting instruments have been widely used to monitor large-scale 20 stationary sources of pollution such as petrochemical plants.

However, in spite of the above advancements in the prior art, there still exists the need in the art for improved chromatography methods and apparatus.

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There is another need in the art for chromatography methods and apparatus for analyzing subterranean fluids.

There is even another need in the art for methods and apparatus for in situ chromatography of subterranean fluids.

These and other needs in the art will become apparent to those of skill in the art upon review of this specification, including its drawings and claims.

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SUMMARY OF THE INVENTION

It is an object of the present invention to provide for improved chromatography methods and apparatus.

It is another object of the present invention to provide for chromatography methods and apparatus for analyzing subterranean fluids.

It is even another object of the present invention to provide for in situ chromatography of subterranean fluids.

These and other objects of the present invention will become apparent to those of skill in the art upon review of this specification, including its drawings and claims.

According to one embodiment of the present invention there is provided an analysis module designed to be positioned in a well bore which includes a chromatograph.

According to another embodiment of the present invention there is provided a method for analyzing formation fluids which includes the steps of: positioning a chromatograph in a well bore; obtaining a sample of formation fluid; introducing the sample into the chromatograph; and processing the data received from the chromatograph to analyze the formation fluid.

According to even another embodiment of the present invention, there is provided a method for analyzing well

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bore fluids. The well bore fluids generally include well fluids added to the well bore and formation fluids from the subterranean formation. The method generally includes adding an isotope marker or tag to a fluid to form a well fluid. The method next includes contacting in the well bore, the well fluid with the formation fluid. The method also includes analyzing the well bore fluid to determine the components of the formation fluid.

According to still another embodiment of the present invention, there is provided a method for analyzing well bore fluids in a well bore. The method generally include positioning a chromatograph in the well bore. The method also includes sampling the well bore fluids, and then analyzing the well bore fluids with the chromatograph.

According to yet another embodiment of the present invention, there is provided an apparatus positioned in a well bore penetrating the subterranean. The apparatus includes a drilling string or umbilical, positioned in the well bore, and extending from the surface into the subterranean. The apparatus also includes a sonde positioned in the well bore, and supported by the drilling string or umbilical, wherein the sonde comprises a chromatograph.

These and other embodiments of the present invention will become apparent to those of skill in the art upon

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review of this specification, including its drawings and claims.

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BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an illustration of a typical drilling operation showing drilling rig 20 and analysis module or logging sonde 100.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a module for the analysis of formation fluid and gas constituents. The purpose of the device is to acquire data down-hole capable of determining the chemical constituents of the sample. This information is used to discriminate among hydrocarbons, determine water salinity, determine oil-water-gas volume fractions, and discriminate between drilling fluids and formation fluids and gases.

Referring now to the figures, FIG. 1 is an illustration of a typical drilling operation showing drilling rig 20 and analysis module or logging sonde 100. Drilling rig 20 is generally a rotary drilling rig which is well known in the drilling art and comprises mast 22 which rises above ground 24. Rotary drilling rig 20 is fitted with lifting gear from which is suspended a drill string 26 formed by a multiplicity of drill pipes 28 screwed into one another having at its lower end a drill bit 32 for the purpose of drilling a well bore 34.

In addition to logging while drilling, module or sonde 100 of the present invention may also be utilized in exploratory logging (i.e., of an open hole), production logging (i.e., of a cased hole), and permanent logging.

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Drilling mud is injected into well bore 34 via the hollow drill pipes 28 of drill string 26. The drilling mud is generally drawn from a mud pit which may be fed with surplus mud from the well bore 34.

5 The analysis module or logging sonde 100 is located in drill string 26 (or alternatively may be supported by an umbilical) in any suitable location and by any suitable manner known to those in the art including by coupling 102 as shown in FIG. 1. Of course, analysis module 100 may be utilized as a stand alone well logging sonde, or may incorporated with other logging instruments 10 in a multi-purpose or multi-task well logging sonde.

15 Of course, well logging sonde 100 must be capable operating in the high pressures of the subterranean at the depths at which it will be operating. Thus, module or sonde 100 will have a housing suitable for 20 withstanding the pressures of the operating depth.

In addition to the physical dimensions, the gas or liquid chromatograph utilized in the present invention 25 must be capable of operation at the temperature and pressure conditions existing at the well bore depth at which it is operating. As non-limiting examples of conditions that might be encountered, include temperatures between about 0°F and about 350°F, and pressures between about 15 PSI and about 15KSI. Of

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course, given the particular operating depth, higher or lower conditions might be encountered.

The electrical power source for the present invention may be provided by a wireline from the surface.

5 If an umbilical is impractical, the power source may be located in analysis module 100 or otherwise be positioned down-hole as long as the power source is of suitable physical dimensions to be utilized in the confines of well bore 34. Non-limiting examples of down-hole power  
10 supplies for module 100 could include a battery system or a down-hole turbine/alternator power supplies as known in the art.

Referring again to FIG. 1, the data received from the analysis module 100 are then processed, by data processor 115 at the well site, and/or simultaneously recorded by recorder 117 for data processing off site, to determine the character of the formation fluid sampled. Preferably, data processor 115 and recorder 117 are a computer with sufficient memory. It is to be understood that data processor 115 may receive data from input sources in addition to the analyzer module of the present invention. It must also be understood that recorder 117 may be any suitable recording device for recording data including tape, diskette, CD, hard drive and the like.  
20 Non-limiting examples of other such data include drill  
25

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bit depth, sampling location, temperature, pressure and mass flow rate.

As is well known in the art, the data processor 115 compares the data the samples obtained by analyzer module 100 to the spectra of standards, prepared of known constituents of known concentrations, or to a database containing a spectrum library in order to determine the molecular constituents of the sample. Software for the analysis of the chromatograph data of mixtures may be purchased commercially or developed specifically for the application.

In operation, the analysis module of the present invention is positioned in the borehole at the proper location to analyze the desired section of the formation. A sample is then acquired, filtered, for particulate matter or compounds, or otherwise processed or stored as desired. The sample, is then introduced into the chromatograph and chemical analysis determined. The sample signal is simultaneously processed and or recorded.

To further aid in distinguishing the formation fluids from the well fluids, a marker or tag may be provided with the well fluid. The relative concentration of this marker or tag in the sample, will provide an estimate of the amount of contribution the well fluid has

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made toward the sample. Knowing the sample composition, the well fluid composition, and the relative contribution of the well fluid to the sample, the formation fluid composition may easily be determined.

5 The present invention includes the use as a tag of an isotope that chemically behaves like or similar to one of the well fluid components, that may be readily distinguished in the gas or liquid chromatography.

10 For example, most commonly, this would include replacement of one or more atoms of hydrogen, carbon or oxygen of one or more of the well fluid components with an isotope will provide an sufficient marker. For example replacing one or more of the atoms of water or a complex hydrocarbon in the well fluid with an isotope. 15 As a specific and preferred example, the use of deuterium as part of or all of the water component of the well fluid.

20 In the operation of a well having a well bore, in which there is present in the well bore fluids both formation fluids and added well fluids, the method of the present invention would include providing a tag or marker to well fluid prior to addition of the well fluid to the well bore, obtaining a sample of well bore fluid, and 25 analyzing the well bore fluid to determine the composition of the formation fluid. Preferably, the tag

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or marker is an isotopic marker, more preferably, deuterium. Also preferably, the analysis of the sample would be by utilizing a chromatograph, and more preferably by utilizing a chromatograph positioned in the well bore, even more preferably, positioned in the well bore at or near the sample depth.

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While the illustrative embodiments of the invention have been described with particularity, it will be understood that various other modifications will be apparent to and can be readily made by those skilled in the art without departing from the spirit and scope of the invention. Accordingly, it is not intended that the scope of the claims appended hereto be limited to the examples and descriptions set forth herein but rather that the claims be construed as encompassing all the features of patentable novelty which reside in the present invention, including all features which would be treated as equivalents thereof by those skilled in the art to which this invention pertains.

All patents, articles, papers, books, and other references cited herein, are herein incorporated by reference for all that they disclose, teach, and reference.

## I CLAIM:

1       1. An analysis module designed to be positioned in a  
2       well bore comprising:

3               (a) a logging sonde;

4               (b) a sampler system supported by the sonde; and

5               (c) a chromatograph supported by the logging sonde  
6       and sized to be positioned in the well bore to receive a  
7       sample having sample components from the sampler system;

8               wherein the chromatograph analyzes the sample by  
9       ionizing the sample into molecular ions and fragment  
10      ions, sorting the molecular ions and fragment ions on the  
11      basis of mass to charge ratio (m/e) and producing a  
12      spectrum unique to the sample components.

1       2. The analysis module of claim 1 wherein the sampler  
2       system further comprises:

3               (d) a drill string or umbilical affixed to the  
4       sonde.

1       3. The analysis module of claim 1 wherein the module  
2       further comprises:

3               (c) a vacuum source.

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1       4. The analysis module of claim 1 wherein the module  
2       further comprises:

3               (c) an electrical power source.

1       5. A method for analyzing formation fluids comprising:

2               (a) positioning a logging sonde comprising a  
3       chromatograph in a well bore;

4               (b) obtaining a sample, having sample components,  
5       of fluid from the wellbore and formation;

6               (c) introducing the sample into the chromatograph  
7       positioned in the well bore.

1       6. The method of claim 5 wherein a particulate matter  
2       removal means removes particulate matter from the sample  
3       prior to introducing the sample into the chromatograph.

1       7. The method of claim 5 wherein the chromatograph  
2       further includes a vacuum source.

1       8. The method of claim 5 wherein the chromatograph  
2       further includes an electrical power source.

1       9. A method for analyzing fluids from a subterranean  
2       formation, the fluids comprising those fluids added to

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3 the well bore and formation fluids from the subterranean  
4 formation, the method comprising:

5 (a) adding an isotope which is not naturally  
6 abundant in the formation or the formation fluid to the  
7 drilling or completion fluid;

8 (b) contacting in a well bore, the formation fluid  
9 potentially contaminated by the drilling or completion  
10 fluid;

11 (c) analyzing the fluid sample could determine the  
12 components of the sample and to ascertain the extent of  
13 contamination by drilling fluid.

1 10. The method of claim 9, wherein the analyzing of step  
2 (c) includes utilizing a chromatograph.

1 11. The method of claim 9, wherein the analyzing of step  
2 (c) includes utilizing a chromatograph positioned in the  
3 well bore.

1 12. A method for analyzing fluids in a well bore, the  
2 method comprising:

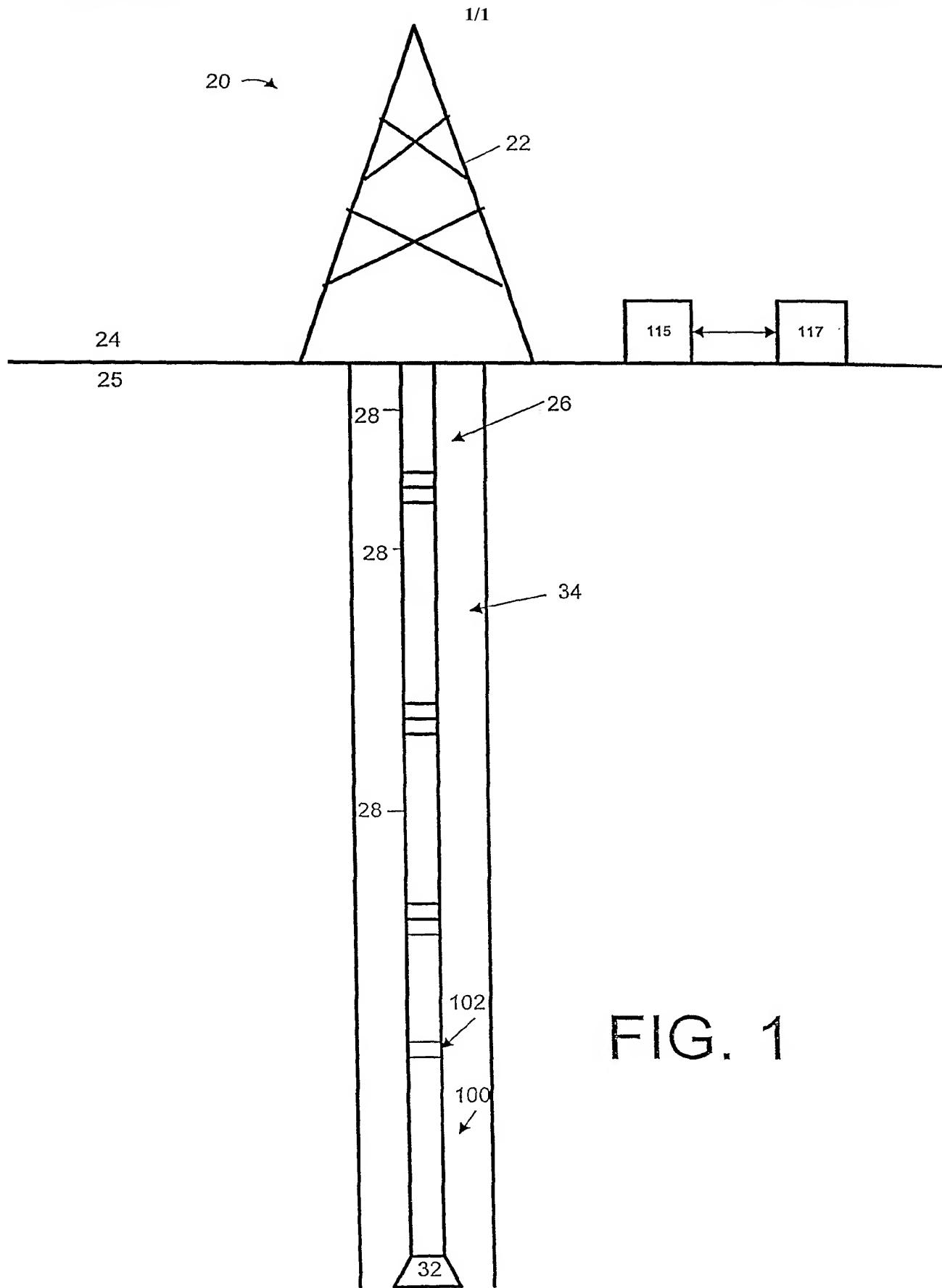
3 (a) positioning a chromatograph in the well bore;  
4 (b) sampling the fluids;  
5 (c) analyzing the fluids with the chromatograph.

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1       13. An apparatus positioned in a well bore penetrating  
2       the subterranean, the apparatus comprising:

3               (a) a drilling string or umbilical, positioned in  
4       the well bore, extending from the surface into the  
5       subterranean;

6               (b) a sonde positioned in the well bore, and  
7       supported by the drilling string or umbilical, wherein  
8       the sonde comprises a chromatograph.



# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/40372

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : G01N 30/62, 33/24  
US CL : 422/70,89; 436/29

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
U.S. : 422/70,89; 436/27,28,29,25,27,30

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
EAST: ((subterranean or "formation fluid" or "formation fluids" or oil\$3 or gas\$3 or petroleum) with chromatogr\$5) with well

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,739,654 A (PILKINGTON et al.) 26 April 1988 (26.04.1988), Abstract, column 2, lines 12-29 and 35-40.	1,2,4-6,8,12,13
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Y		3, 7, 9-11
Y	US 4,474,889 A (TERRY et al.) October 2, 1984 (10.02.1984), column 3, lines 18-21	3, 7
Y	US 4,420,565 A (SCHMITT) 13 December 1983 (03.12.1983), column 1, lines 35-40	9-11

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:		
"A" document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"O" document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed		

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17 July 2001 (17.07.2001)

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